Synthesis and chiral recognition ability of helical polyacetylenes bearing helicene pendants

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[*Note*]

Synthesis and Chiral Recognition Ability of Helical Polyacetylenes Bearing Helicene Pendants

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Abstract: Novel polyacetylenes bearing an optically active or racemic [6]helicene unit as the pendant groups directly bonded to the main-chain (poly-**1**s) were prepared by the polymerization of the corresponding acetylenes (**1**-*rac*, **1**-*P*, and **1**-*M*) with a rhodium catalyst. The optically active polyacetylenes (poly-**1**-*P* and poly-**1**-*M*) formed a preferred-handed helical conformation biased by the optically active helicene pendants, resulting in the induced circular dichroism (ICD) in their π-conjugated polymer backbone regions. The optically active helical polymers, when employed as an

enantioselective adsorbent, showed a high chiral recognition ability towards racemates, such as the monomeric [6]helicene and 1,1’-binaphthyl analogues, and enantioselectively adsorbed one of the enantiomers.

Keywords: helicene / polyacetylene / helical structure / chirality / chiral recognition

INTRODUCTION

Helicenes are unique polycyclic aromatic compounds and are inherently chiral because of their nonplanar screw-shaped skeletons.[1] Due to such intriguing features of the helicenes that involve helical chirality, conjugated π-systems, and fluorescent and chiroptical properties,[1,2] optically active helicene-containing polymers have the potential to be applied to a wide range of material sciences including optoelectric materials, asymmetric catalysts, and chiral separation and sensing materials. To date, several groups have attempted to introduce helicene units into macromolecules,[3] but the applications of optically active helicene-containing polymers as chiral materials are quite limited.[1a,b,e] In particular, the application of optically active helicene-containing polymers as enantioselective adsorbents and chiral stationary phases (CSPs) for high-performance liquid chromatography (HPLC) has not been reported previously, in spite of the recent significant advance in chromatographic enantioseparation that has become an essential technique for the development of chiral drugs in the pharmaceutical industry.[4]

On the other hand, the development of artificial helical polymers with a controlled helical sense has advanced considerably during the past decades because of their possible applications to chiral materials.[5] Among the synthetic helical polymers prepared so far, polyacetylenes are one of the most extensively studied helical polymers,[5,6] and some of them have been successfully utilized as asymmetric catalysts[7] and chiral adsorbents[8] and CSPs,[9,10] where the preferred-handed helical structures appear to be dispensable for their enantioselectivities and resolving abilities, respectively.

We anticipated that an optically active [6]helicene derivative might be a suitable chiral component as the pendant group to develop a novel optically active helical polyacetylene, since the helicene residues, once introduced covalently to the polyacetylene backbone, could induce a preferred-handed helical structure in the polymer accompanied by a one-handed helical array of the helicene pendants, thus showing an intriguing chiral recognition ability originating from the helical chiralities of the helicene itself and polymer main-chain as well. To this end, we have designed and

synthesized a series of novel optically inactive (poly-**1**-*rac*) and active polyacetylenes (poly-**1**-*P* and poly-**1**-*M*) (Scheme 1) bearing an racemic or optically active helicene unit as the pendant groups directly connected to the polymer backbone, and also investigated the chiroptical properties of poly-**1**-*P* and poly-**1**-*M* and their chiral recognition abilities evaluated on the basis of an enantioselective adsorption method toward several racemates.[11]

RESULTS AND DISCUSSION

The helicene monomer 2-ethynyl-carbo[6]helicene (**1**-*rac*) was prepared and resolved into the enantiomers by chiral HPLC separation according to the previously reported method[2h] (**1**-*P* and **1**-*M* with right- and left-handed screw senses, respectively; enantiomeric excess (ee) > 99%) (Supporting Information).

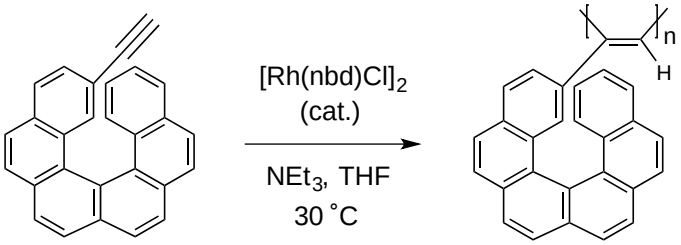
Helically twisted helicene molecules are known to form self-associated supramolecular aggregates through noncovalent, face-to-face π–π interactions, which frequently triggers spontaneous resolution; *P*- and *M*-helicenes favorably form homochiral assemblies over heterochiral ones due to a greater π–π overlap between the helicenes with the same configuration.[1a,b,e,12] If this is the case, we anticipated that the enantiomerically pure **1**-*P* and **1**-*M* could polymerize faster than its racemic mixture (**1**-*rac*), giving higher molecular weight (MW) homochiral polymers (poly-**1**-*P* and poly-**1**-*M*, respectively) or the racemic **1**-*rac* could polymerize in a stereoselective manner (poly-**1**-*rac*) via a growing chain-end control mechanism, thus producing a mixture of polymers rich in either **1**-*P* or **1**-*M*.[13]

In order to investigate this possibility, we first polymerized **1**s on a small scale under various conditions, namely in different solvents (tetrahydrofuran (THF) and chloroform) in the presence of NEt_3, different concentrations of **1**s (0.02 – 0.2 M) and rhodium catalysts (1 – 6 mol%) (neutral $[Rh(nbd)Cl]_2$ and cationic $[Rh(nbd)_2BF_4]$ (nbd: norbornadiene), respectively) based on the previously reported results.[14] However, the polymers precipitated during the polymerizations

independent of the conditions, affording polymers with a relatively small MW in moderate yields. Therefore, the difference in the polymerization reactivity between **1**-*rac* and **1**-*P* or **1**-*M* was difficult to investigate.

Typical polymerization results in THF in the presence of NEt_3 using $[Rh(nbd)Cl]_2$ as a catalyst, yielding stereoregular (cis-transoidal) polyacetylenes,[15] poly-**1**-*rac,* poly-**1**-*P*, and poly-**1**-*M* (Scheme 1), are shown in Table 1 (entries 1–3, 4, 9, and 14). The number-average molecular weights (M_n) of poly-**1**-*P* and poly-**1**-*M* (M_n = 2.6 x 10^3) were higher than that of poly-**1**-*rac* (M_n = 1.6 x 10^3) (entries 1–3). However, this tendency was not reproducible (see entries 4, 9, and 14 in Table 1), because the polymers precipitated during the polymerization as mentioned above. The size exclusion chromatography (SEC) profiles of poly-**1**s showed multimodal peaks, thus we fractionated poly-**1**s (Table 1, entries 4, 9, and 14) into four fractions (indicated by a subscript notation using A–D) due to MW by SEC (Figure S4 and Table 1)[17] and their chiroptical properties were investigated.

Scheme 1. Rhodium-Catalyzed Polymerization of **1**



1-*rac*
1-*P*
1-*M*

poly-**1**-*rac*
poly-**1**-*P*
poly-**1**-*M*

Table 1. Polymerization of 1-*rac*, 1-*P*, and 1-*M* with $[Rh(nbd)Cl]_2$ and SEC Fractionation Results of Poly-1-*rac*, Poly-1-*P*, and Poly-1-*M*[a]

		polymer					
entry	monomer	code	yield (%)	M_n x 10^{-3}	M_w/M_n[d]	$\Delta\varepsilon_{1\sigma\tau}$	$\Delta\varepsilon_{2\nu\delta}$ M^{-1} cm^{-1}
1	**1**-*rac*	poly-**1**-*rac*	50	1.6	3.4	–	–
2[b]	**1**-*P*	poly-**1**-*P*	25	2.6	5.3	0.98	–0.88
3	**1**-*M*	poly-**1**-*M*	17	2.6	7.1	–0.94	0.82
4[c]	**1**-*rac*	poly-**1**-*rac*	46	1.8	3.6	–	–
5		poly-**1**-rac_A	–	5.8	2.0	–	–
6		poly-**1**-rac_B	–	11	1.3	–	–
7		poly-**1**-rac_C	–	3.0	1.6	–	–
8		poly-**1**-rac_D	–	0.74	1.1	–	–
9[c]	**1**-*P*	poly-**1**-*P*	52	1.7	2.7	1.22	–1.13
10		poly-**1**-P_A	–	–[e]	–[e]	–[e]	–[e]
11		poly-**1**-P_B	–	7.0	1.4	1.27	–1.12
12		poly-**1**-P_C	–	2.7	1.3	1.29	–1.14
13		poly-**1**-P_D	–	0.73	1.4	1.32	–1.25
14[c]	**1**-*M*	poly-**1**-*M*	47	1.8	2.7	–1.16	1.07
15		poly-**1**-M_A	–	–[e]	–[e]	–[e]	–[e]
16		poly-**1**-M_B	–	5.2	1.3	–1.24	1.07
17		poly-**1**-M_C	–	2.1	1.6	–1.25	1.10
18		poly-**1**-M_D	–	0.79	1.4	–1.31	1.23

[a]Polymerized under nitrogen; [monomer] = 0.2 M, [Rh]/[monomer] = 100. [b][Rh]/[monomer] = 33. [c][Rh]/[monomer] = 17. [d]Determined by SEC (polystyrene standards) with THF as the eluent. [e]Not measured because the amounts of poly-**1**-P_A and poly-**1**-M_A obtained by SEC fractionation were too small.

Figure 1A shows the circular dichroism (CD) and absorption spectra of optically active **1**-*P*, **1**-*M*, poly-**1**-P_B, and poly-**1**-M_B measured in THF at 25 ˚C. The monomers **1**-*P* and **1**-*M* gave rise to the typical absorption signals centered at around 270 and 320 nm assigned to the helicene moiety (g and h in Figure 1A) and characteristic intense Cotton effects in the regions (c and d).[2h] On the other hand, poly-**1**-P_B and poly-**1**-M_B showed an apparent CD in the π-conjugated main-chain region (380–600 nm) induced by the chiral helicene pendants as well as CDs in the helicene chromophore region (235–380 nm) (a and b), whose CD spectral patterns were different from those of the monomers **1**-*P* and **1**-*M*. Figure 1B shows the differential CD spectra, where the contributions arising from the CD absorption due to the enantiomerically pure **1**-*P* and **1**-*M* themselves are subtracted from the observed CD spectra of the poly-**1**-P_B and poly-**1**-M_B, respectively **(**i and j in Figure 1B**)**. The differential CD spectral patterns seem to be like those of helical polyacetylenes with optically active pendant groups,[18] suggesting that poly-**1**-*P* and poly-**1**-*M* most likely possess an excess of a one-handed helical conformation induced by the optically active helicene pendants, which may further result in a preferred-handed helical array of the helicene pendants along the single-handed helical polymer backbone.

The CD and absorption spectra of fractionated poly-**1**-$P_{C,D}$ and poly-**1**-$M_{C,D}$ were also measured in THF at 25 ˚C (Figure S5A, C, D), which, together with the differential CD spectra (Figure S5B), indicated that the CD intensities more or less depended on the MW of the polymers, but their difference was not significant, probably because poly-**1**-*P* and poly-**1**-*M* likely possess a rather stable helical conformation with an excess one-handedness stabilized by the attractive intramolecular π–π interaction between the helically arranged helicene pendants with the same configuration. This speculation was supported by the facts that the CD spectra of poly-**1**-$P_{B,C}$ and poly-**1**-$M_{B,C}$ hardly changed over the temperature range of -10 – 55 ˚C in THF and remained unchanged after heating at 55 ˚C for 2 h (Figure S6). Such a thermal stability of the present helical poly-**1**-*P* and poly-**1**-*M* is noticeable, since most of the reported helical polyacetylenes are dynamic

in nature and highly sensitive to temperature, which frequently exhibits an inversion of the macromolecular helicity with temperature.[5d,6a,c,f]

Figure 2A,B displays a possible right-handed helical structure of poly-**1**-*M* (20 mer) calculated by molecular mechanics calculations based on a 23 unit/10 turn (23/10) helical poly(phenylacetylene) whose helical structure was determined by X-ray diffraction measurements (see Supporting Information).[19] The calculated structure revealed that the helicene pendant units are closely packed to each other and the neighboring helicene pendant units are overlapped via π–π interactions, resulting in the formation of the one-handed helical array along the helical polymer backbone.[20]

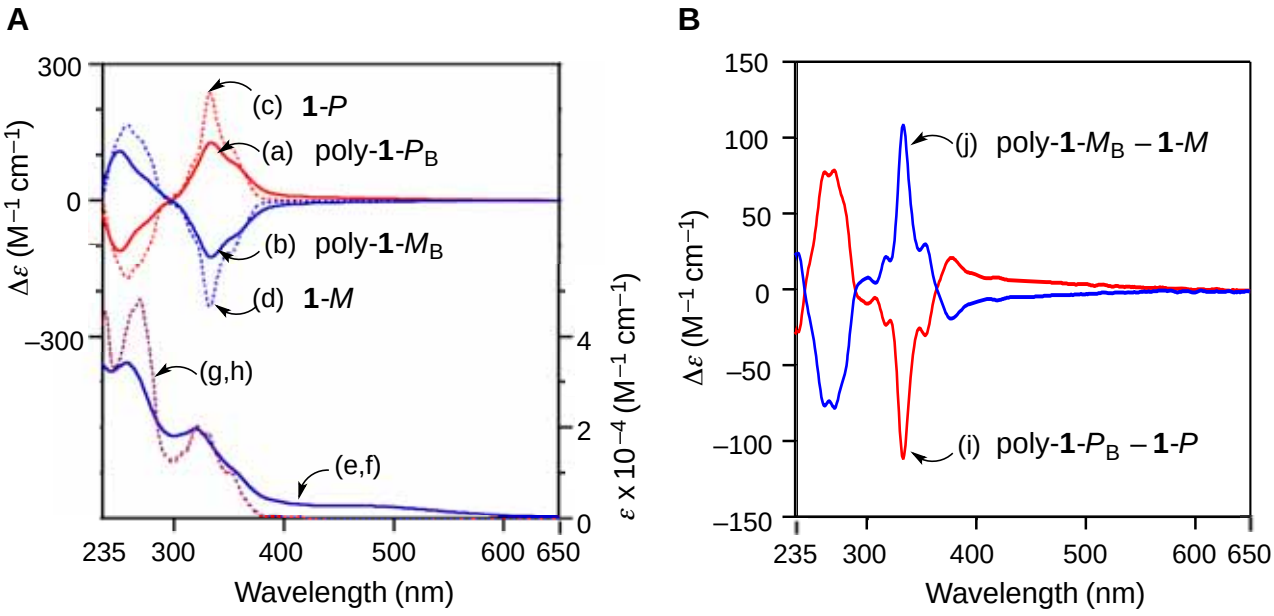


Figure 1. (A) CD (a-d) and absorption (e-h) spectra of poly-**1**-P_B (a,e), poly-**1**-M_B (b,f), **1**-*P* (c,g), and **1**-*M* **(**d,h**)** measured in THF at 25 ˚C. (B) Differential CD spectra between poly-**1**-P_B and **1**-*P* (i) and poly-**1**-M_B and **1**-*M* **(j)**. The concentrations of polymers and monomers were 0.02 and 0.1 mg/mL, respectively.

Figure 2. (A) Side view and (B) top view of a possible right-handed helical structure of poly-**1**-*M* (20 mer). The structure is shown using the space-filling model; the main-chain atoms are shown in yellow for clarity. The pendant helicene residues are arranged in a left-handed helical array along the right-handed helical poly-**1**-*M* backbone. The helix-sense of the main-chain is assumed from the Cotton effect sign in the main-chain region (>380 nm) according to the literature.[18]

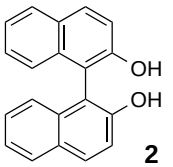
Next, we investigated if the racemic **1**-*rac* could polymerize in a stereoselective fashion to produce a mixture of poly-**1**s rich in either **1**-*P* or **1**-*M* by an enantioselective adsorption technique[11] using optically active (–)-poly(triphenylmethyl methacrylate) ((–)-PTrMA) with a one-handed helical conformation.[5a-c,23] The optically active helical PTrMA is a practically useful chiral packing material for HPLC and has been used to resolve a variety of aromatic racemic compounds including [6]helicene as well as racemic helical polymers such as (±)-PTrMA.[5a-c,24] In fact, (–)-PTrMA selectively adsorbed poly-**1**-*M* from an equimolar mixture of poly-**1**-*P* and poly-**1**-*M* in hexane/THF (80:20, v/v), and its supernatant solution exhibited a CD whose spectral pattern and intensity were identical to that of poly-**1**-*P* (ee = 36.5 %) (for more detailed experimental procedures, see Supporting Information, Table S1, and Figure S7). In the same way, the enantioselective adsorption experiment was performed for poly-**1**-*rac* with (–)-PTrMA. However, the supernatant solution showed almost no CD due to poly-**1**-*P* or poly-**1**-*M* (Table S1 and Figure S7), suggesting that **1**-*rac*

polymerized in an almost random way, or a highly stereoselective polymerization may not occur during the present polymerization of **1**-*rac*.

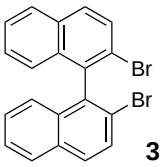
The chiral recognition ability of optically active poly-**1**-*P* and poly-**1**-*M* was then investigated for the aromatic racemic compounds (**1**– **3**) including **1**-*rac* by enantioselective adsorption experiments (Table 2 and Supporting Information).[11,25,26]

Table 2. Enantioselective Adsorption of Racemates on Poly-1-*P* and Poly-1-*M*[a]

entry	analyte	polymer	yield of adsorbed analyte (%) [b]	ee of adsorbed analyte (%) [b]	separation factor (α) [c]
1	**1**	poly-**1**-*P*	5.0	3.6 (*P*)	1.08
2[d]		poly-**1**-*M*	5.0	3.7 (*M*)	1.08
3[d]	**2**	poly-**1**-*P*	0.64	37 (*S*)	2.18
4[d]		poly-**1**-*M*	0.66	35 (*R*)	2.09
5[d]	**3**	poly-**1**-*P*	2.1	26 (*S*)	1.71
6[d]		poly-**1**-*M*	2.3	29 (*R*)	1.84



2



3

[a]Experimental conditions for entries 1 and 2: poly-**1**-*P* or poly-***1***-*M* 2.0 mg; analyte 0.04 mg (1 mL portion from a 0.04 mg/mL solution in methanol). Experimental conditions for entries 3-6: poly-**1**-*P* 2.0 mg or poly-***1***-*M* 3.5 mg; analyte 0.4 mg for poly-**1**-*P* or 0.7 mg for poly-***1***-*M* (1 mL or 1.75 mL portion from a 0.4 mg/mL solution in methanol). [b]Determined by chiral HPLC analysis of analytes adsorbed on poly-**1**-*P* or poly-***1***-*M* using a UV-visible detector. [c]Calculated according to the equation $\alpha = (F_{major}\ (\%)/F_{minor}\ (\%))/(A_{major}\ (\%)/A_{minor}\ (\%))$, where F_{major} and F_{minor} are the percentages of major and minor enantiomers of free analyte in the supernatant solutions, respectively, and A_{major} and A_{minor} are those of major and minor enantiomers of adsorbed analyte, respectively. [d]Average values of two runs.

The poly-**1**-*P* and poly-**1**-*M* selectively adsorbed one of the enantiomers of **1** – **3** in methanol. The adsorbed analytes on the polymers were almost completely recovered by desorption in

methanol and subsequently in a methanol/THF (50:50, v/v) mixture (Supporting Information), and their amounts and ee values were estimated by chiral HPLC analysis (Table 2).

As anticipated,[1a,b,e,12] poly-**1**-*P* and poly-**1**-*M* preferentially adsorbed **1**-*P* and **1**-*M* with the same configuration of the helicene residues, furnishing 3.6 and 3.7 % ee, respectively (entries 1 and 2). Interestingly, poly-**1**-*P* and poly-**1**-*M* showed a much better and remarkable chiral recognition toward the racemic 1,1'-binaphthyl analogues (**2** and **3**), and selectively adsorbed the (*S*)- and (*R*)-enantiomers, respectively, with up to 37 % ee (entries 3-6). On the basis of the amounts and ee values of the analytes (**1 – 3**) adsorbed on the polymers, the separation factor (α), which is a useful measure in chiral HPLC to evaluate the chiral resolving ability of optically active hosts toward racemic analytes[11] can be calculated (Table 2).[4] The calculated α values (1.71 ~ 2.18) are high enough for the complete separation of enantiomers when used as a CSP for HPLC,[4,5a,b] indicating the helicene-bound helical polyacetylenes possesses a practically useful chiral recognition power for aromatic racemic compounds like a commercially available (+)-PTrMA column.

The enantioselective adsorption results on the poly-**1**-*P* and poly-**1**-*M* (Table 2) revealed insight into the chiral recognition mechanism, in other words, the stereochemistry of poly-**1**–analyte interaction; helically arranged helicene-pendant residues along the poly-**1** helical backbone (Figure 2) appear to be responsible for the observed efficient separation of aromatic analytes (**1 – 3**). The two naphthyl rings of the more retained enantiomers of (*R*)-**2** and (*R*)-**3** on poly-**1**-*M* may be favorably twisted into a left-handed helix so as to interact with the adjacent *M*-helicene groups arranged in a left-handed helical array through the aromatic interactions, whereas due to a considerable π–π overlap between the helicene pendants may interfere with favorable close helicene-helicene interactions between poly-**1** and **1**-*rac*, resulting in a relatively lower separation factor than we anticipated.

CONCLUSIONS

In summary, we have, for the first time, prepared stereoregular helical polyacetylenes bearing optically active and racemic [6]helicene groups as the pendants. Although the molecular weights of the polymers were rather low because of the low solubility of the helicenes, the optically active helicene-bound polymers exhibited an apparent CD in the polymer backbone chromophore region due to a preferred-handed helix formation biased by the chiral helicene residues. Moreover, we found that the optically active helicene-bound polyacetylenes showed a high chiral recognition ability toward racemic 1,1'-binaphthyl derivatives largely arising from a one-handed helical array of the pendant helicene residues.

The present results suggest that a more practically useful chiral material for separation of enantiomers may be developed based on analogous helicene- and organometallic helicene[2f]-bound helical polyacetylenes by introducing a long alkyl chain on the helicene residue, which will overcome the solubility problem of polymers, thereby providing a unique chiral stationary phase with high enantioselectivity composed of one-handed helical polyacetylenes with screw-shaped helicene and organometallic helicene pendants, and further studies along this line are now in progress.

Supporting Information. Experimental details in the synthesis and characterization of poly-**1**s and the enantioselective adsorption on poly-**1**-*M* and poly-**1**-*P*, and the molecular modeling and calculations of poly-**1**-*M*. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) A series of [4]helicene-based oligomers enabling to form self-aggregates where the chirality of the helicene units significantly affects the self-assembly has also been reported.[1a,3i,12c]

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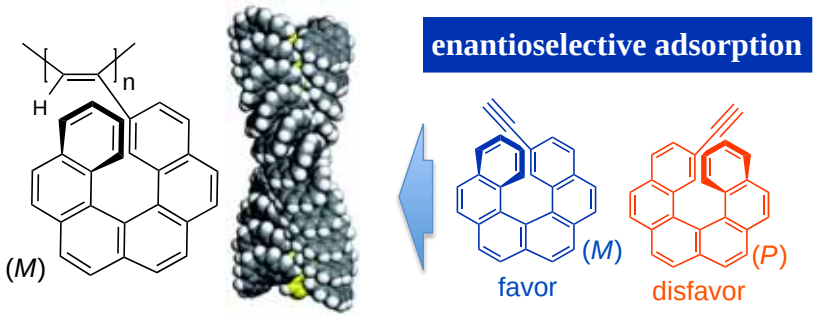
Synthesis and Chiral Recognition Ability of Helical Polyacetylenes Bearing Helicene Pendants

Emmanuel Anger, Hiroki Iida, Tomoko Yamaguchi, Kotaro Hayashi, Daisuke Kumano, Jeanne Crassous,* Nicolas Vanthuyne, Christian Roussel, and Eiji Yashima*



Supporting Information for:

Synthesis and Chiral Recognition Ability of Helical Polyacetylenes Bearing Helicene Pendants

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1. Instruments

The NMR spectra were measured using a Varian AS500 spectrometer (Agilent, Santa Clara, CA) operating at 500 MHz for ^{1}H using tetramethylsilane (TMS) as the internal standard. The absorption and CD spectra were obtained in a 0.1, 0.5, or 5 cm quartz cell using a JASCO V570 spectrophotometer and a JASCO J-820 spectropolarimeter, respectively (JASCO, Tokyo, Japan). The temperature was controlled with a JASCO PTC-423L apparatus. The concentrations of the polymers were calculated based on the monomer units. The size exclusion chromatography (SEC) measurements and fractionations were performed with a JASCO PU-980 liquid chromatograph equipped with a UV-visible detector (300 nm, JASCO UV-1570) and a column oven (JASCO CO-1565). The number-average molecular weight (M_n) and its distribution (M_w/M_n) were determined at 40 °C using a Tosoh TSKgel Multipore H_{XL}-M (0.78 (i.d.) x 30 cm) SEC column (Tosoh, Tokyo, Japan), and tetrahydrofuran (THF) or chloroform ($CHCl_3$) was used as the eluent at a flow rate of 0.5 or 1.0 mL/min, respectively. The molecular weight calibration curve was obtained with polystyrene standards (Tosoh). The chiral HPLC analyses and separations were performed on a JASCO PU-2080 liquid chromatograph equipped with a UV-visible detector (JASCO UV-2075 or MD-2010) and an optical rotation (JASCO OR-2090) or a CD detector (JASCO CD-2095) using Chiracel OD-H, Chiralpak IA, and Chiralpak IB columns (0.46 (i.d.) x 25 cm, or 2 (i.d.) x 25 cm, Daicel, Osaka, Japan). The laser Raman spectra were taken on a JASCO RMP-200 spectrophotometer.

2. Materials

All starting materials and anhydrous solvents were purchased from Aldrich (Milwaukee, WI), Wako Pure Chemical Industries (Osaka, Japan), or Tokyo Kasei (TCI, Tokyo, Japan), and were used as received, except for triethylamine (Et_3N) and THF. Et_3N was dried over KOH pellets and distilled onto KOH under nitrogen. THF was dried and deoxygenized by passing through purification columns (Glass Contour Solvent System, Nikko Hansen, Osaka, Japan), distilled onto $LiAlH_4$ under nitrogen, and redistilled under high vacuum just before polymerization. 2-Ethynyl-carbo[6]helicene (**1**-*rac*) was synthesized according to the previously reported method.[S1] The helicene **1**-*rac* was separated into the enantiomers (**1**-*P* and **1**-*M*) using a chiral HPLC column (Chiralpak IB, 2 (i.d.) x 25 cm, *n*-hexane/EtOH = 99:1 (v/v), 11 mL/min), and the enantiomeric excess (*ee*) values of the **1**-*P* and **1**-*M* separated were estimated to be >99% using a chiral HPLC column (Chiralpak IB, 0.46 (i.d.) x 25 cm, *n*-hexane/EtOH = 99:1 (v/v), 1 mL/min) (Figure S1). (–)-Poly(triphenylmethyl methacrylate) (PTrMA, $[\alpha]_D^{25}$ -336 (*c* 2.0, THF)) was synthesized according to the previously reported method.[S2] The M_n and M_w/M_n of

(–)-PTrMA estimated as its methyl ester (poly(methyl methacrylate) were 7.0 x 10^3 and 1.19, respectively, as determined by SEC using poly(styrene) standards in $CHCl_3$ as the eluent.

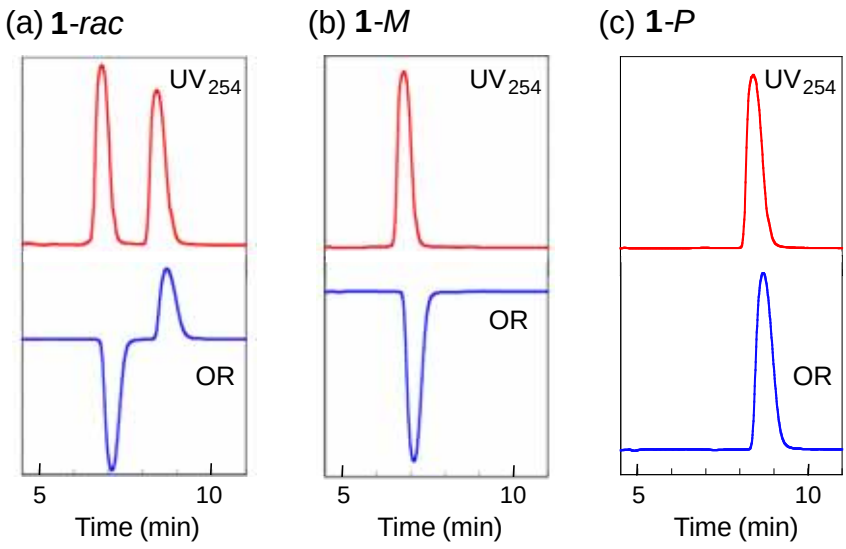

Figure S1. HPLC traces of **1**-*rac* (a), **1**-*M* (b), and **1**-*P* (c) using a Daicel Chiralpak IB column [*n*-hexane/EtOH = 99:1 (v/v), 1 mL/min].

3. Synthesis of Polymers

Polymerization. Polymerizations of **1**-*rac*, **1**-*P*, and **1**-*M* were carried out according to Scheme 1 in a dry glass ampule under a dry nitrogen atmosphere using $[Rh(nbd)Cl]_2$ as a catalyst in a similar way as reported previously.[S3] The polymerization results are summarized in Table 1. A typical polymerization procedure is described below.

The monomer **1**-*M* (50.0 mg, 0.142 mmol) was placed in a dry ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation-flush procedure was repeated three times, a three-way stopcock was attached to the ampule, and a mixture of Et_3N (19.8 μL, 0.142 mmol) and anhydrous THF (0.64 mL) was added with a syringe. To this was added a solution of $[Rh(nbd)Cl]_2$ (0.06 M) in THF (0.07 mL) at 30 °C. The concentrations of the monomer and the rhodium catalyst were 0.2 and 0.006 M, respectively. After 13 h, a solution of $[Rh(nbd)Cl]_2$ (0.06 M) in THF (0.07 mL) was added again to complete the polymerization. After additional 5 h, the resulting polymer (poly-**1**-*M*) was precipitated into a large amount of Et_2O, washed with Et_2O, and collected by centrifugation. The product was purified by reprecipitation from $CHCl_3$ to Et_2O, and the precipitated poly-**1**-*M* was washed with

Et_2O and dried *in vacuo* at room temperature overnight (23.6 mg, 47% yield) (entry 4 in Table 1). The M_n and M_w/M_n values were 1.8×10^3 and 2.7, respectively, as determined by SEC using polystyrene standards in THF as the eluent. The obtained poly-**1**-*M* (12 mg) was then subjected to SEC fractionation to obtain four parts with different molecular weights, poly-**1**-M_A (<0.1 mg), poly-**1**-M_B (ca. 4 mg, M_n = 5.2 x 10^3, M_w/M_n = 1.3, poly-**1**-M_C (ca. 4 mg, M_n = 2.1 x 10^3, M_w/M_n = 1.6), and poly-**1**-M_D (ca. 4 mg, M_n = 0.79 x 10^3, M_w/M_n = 1.4). The results of the SEC fractionation are summarized in Table 1.

Spectroscopic data of poly-**1**-*M* (entry 14 in Table 1): IR (film, cm^{-1}) 3045, 2920, 2850. ^1H NMR (500 MHz, $CDCl_3$, 50 °C): δ 8.0 (br, aromatic, C=CH). Anal. Calcd (%) for $(C_{28}H_{16})_n$: C, 95.42; H, 4.58. Found: C, 95.61; H, 4.79.

Spectroscopic data of poly-**1**-*rac* (entry 4 in Table 1): Yield: 46%. IR (film, cm^{-1}) 3045, 2918, 2849. ^1H NMR (500 MHz, $CDCl_3$, 50 °C): δ 8.0 (br, aromatic, C=CH). Anal. Calcd (%) for $(C_{28}H_{16})_n$: C, 95.42; H, 4.58. Found: C, 95.41; H, 4.70.

Spectroscopic data of poly-**1**-*P* (entry 9 in Table 1): Yield: 52%. IR (film, cm^{-1}) 3044, 2917, 2849. ^1H NMR (500 MHz, $CDCl_3$, 50 °C): δ 8.0 (br, aromatic, C=CH). Anal. Calcd (%) for $(C_{28}H_{16})_n$: C, 95.42; H, 4.58. Found: C, 95.32; H, 4.58; N, 0.14.

4. Characterization of Monomers and Polymers

The ^{1}H NMR spectra of poly-**1**s were too broad to determine the stereoregularity. Therefore, their stereoregularities were investigated by laser Raman spectroscopy. Figure S2 shows the Raman spectra of poly-**1**-*rac*, poly-**1**-*P*, and poly-**1**-*M* (Table 1, entries 4, 9, and 14). All the polymers showed intense peaks at 1505, 1311, 873 cm^{-1} (a), 1509, 1310, 882 cm^{-1} (b), and 1508, 1311, 874 cm^{-1} (c), which can be assigned to the C=C, C-C, and C-H bond vibrations in the *cis* polyacetylenes, respectively,[S4] indicating that these polymers possess a highly *cis-transoidal* structure.

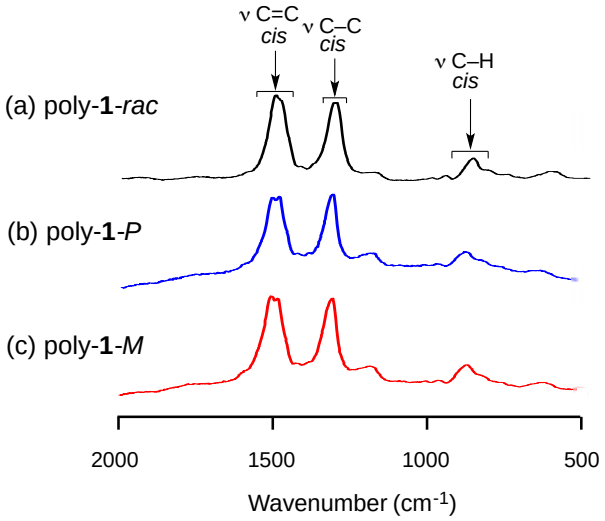

Figure S2. Raman spectra of poly-**1**-*rac* (a), poly-**1**-*P* (b), and poly-**1**-*M* (c).

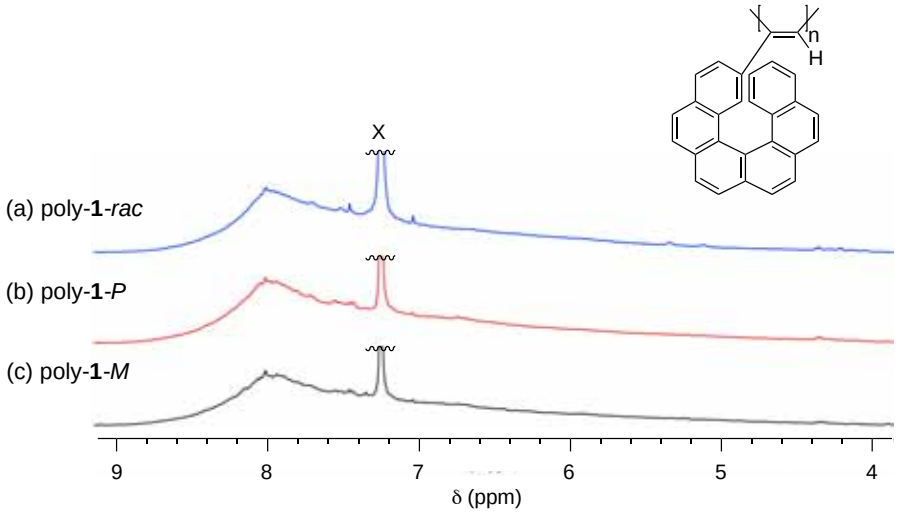

Figure S3. ^{1}H NMR spectra of poly-**1**-*rac* (a), poly-**1**-*P* (b), and poly-**1**-*M* (c) in $CDCl_3$ at 50 ˚C. X denotes the proton from $CHCl_3$.

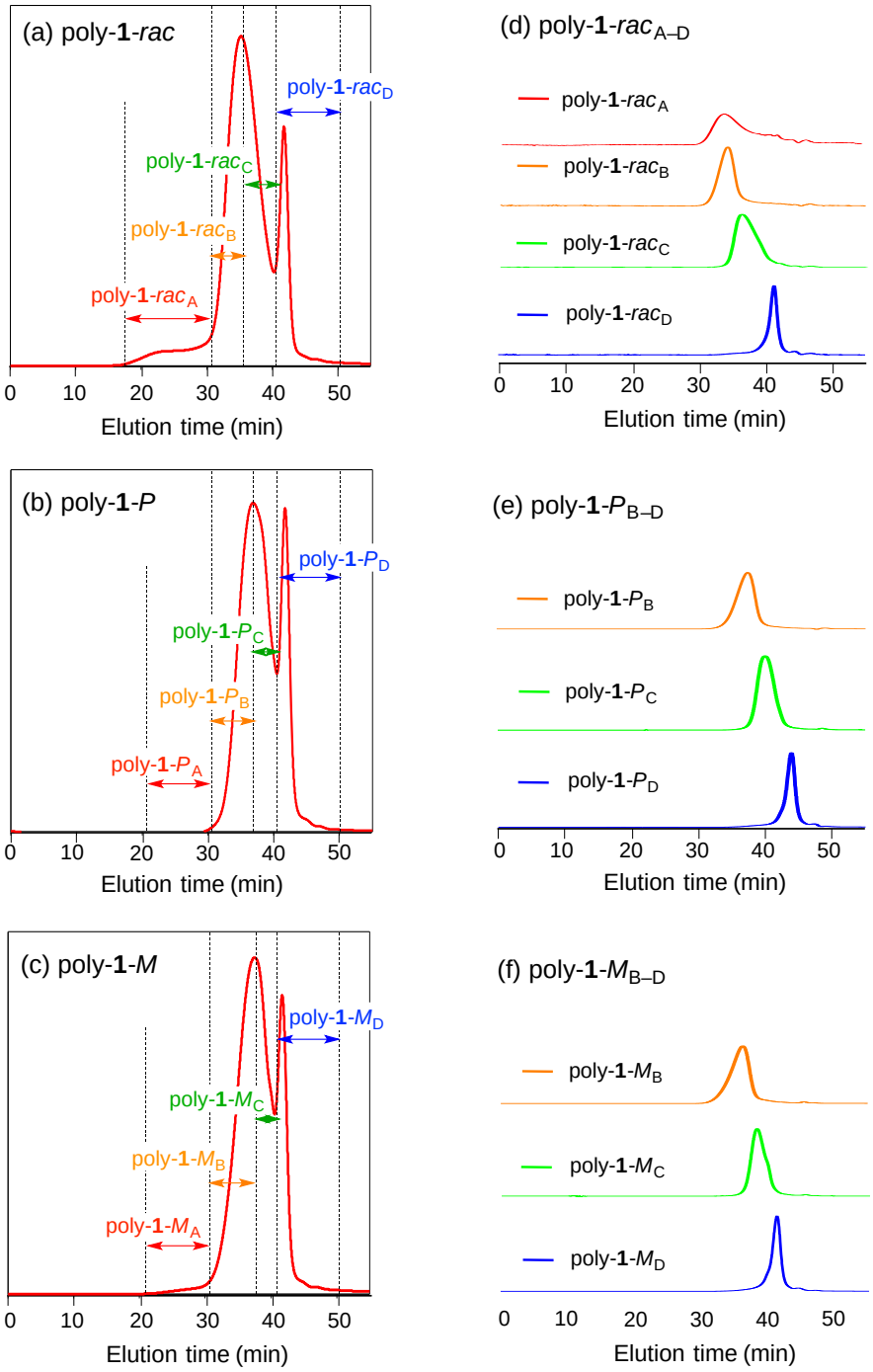

Figure S4. SEC chromatograms of poly-**1**-*rac* (a), poly-**1**-*P* (b), poly-**1**-*M* (c), poly-**1**-*rac*$_{A–D}$ (d), poly-**1**-$P_{B–D}$ (e), and poly-**1**-$M_{B–D}$ (f) at 40 °C (column, TSKgel Multipore H_{XL}-M (0.78 (i.d.) x 30 cm; eluent, THF; flow rate, 0.5 mL/min).

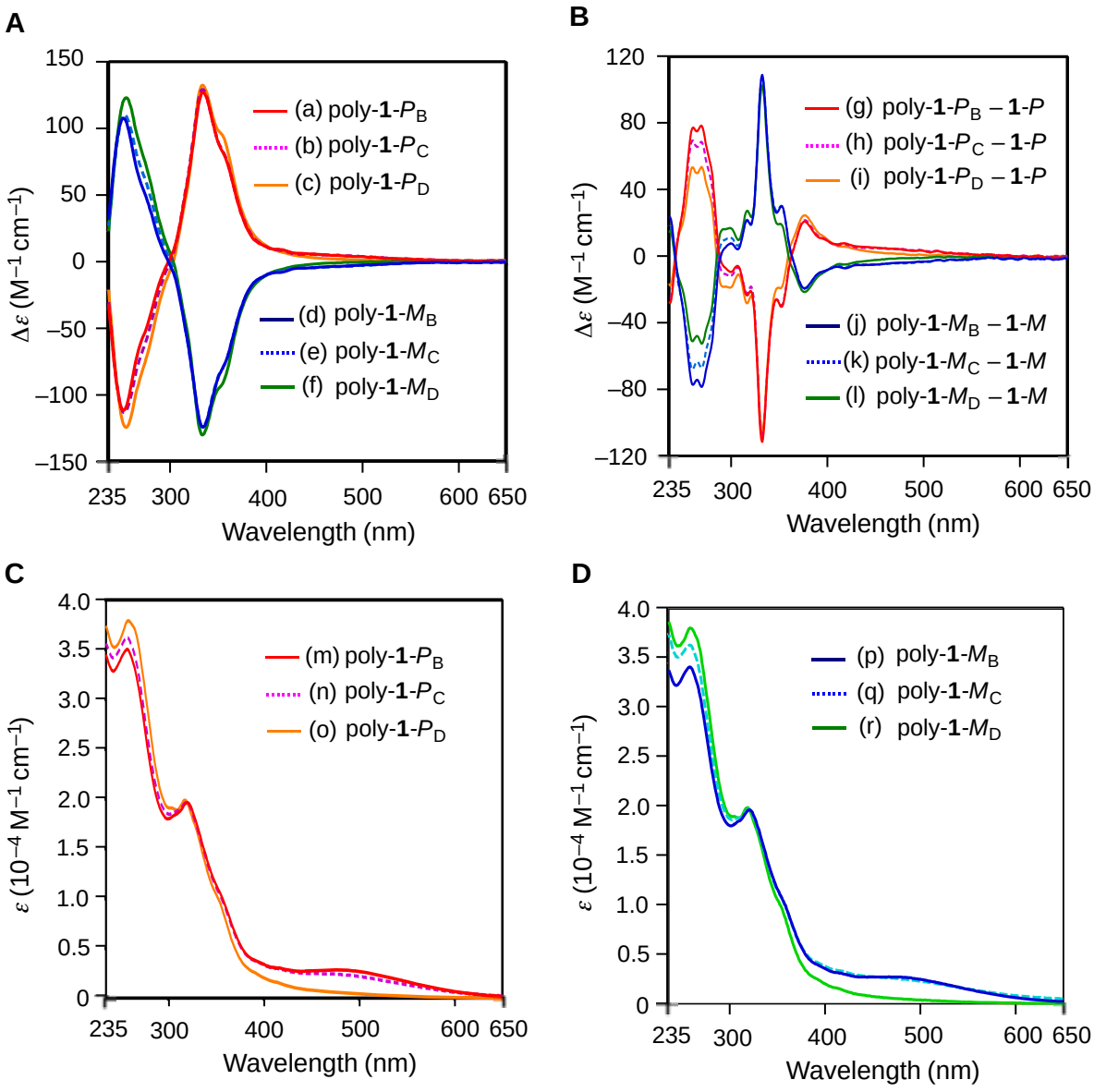

Figure S5. (A) CD and (C, D) absorption spectra of fractionated poly-**1**-$P_{B\text{-}D}$ (a-c, m-o) and poly-**1**-$M_{B\text{-}D}$ (d-f, p-r) in THF at 25 ˚C. (B) Differential CD spectra between fractionated poly-**1**-$P_{B\text{-}D}$ and **1**-*P* and poly-**1**-$M_{B\text{-}D}$ and **1**-*M* (see also Figure 1). The concentrations were 0.02 mg/mL.

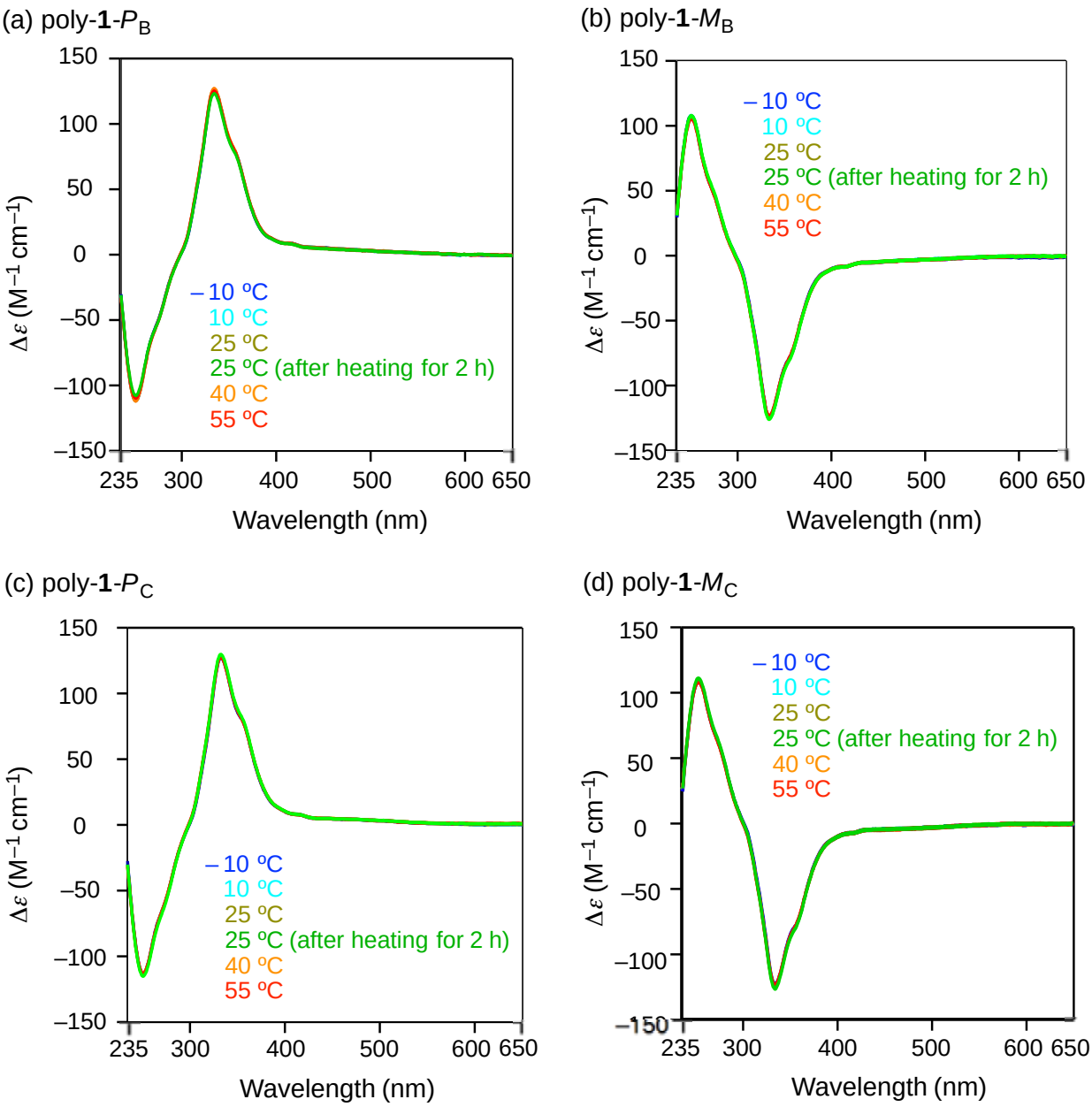

Figure S6. CD spectra of poly-**1**-P_B (a), poly-**1**-M_B (b), poly-**1**-P_C (c), and poly-**1**-M_C (d) in THF (0.02 mg/mL) at various temperatures and at 25 °C after heating at 55 °C for 2 h.

5. Molecular Modeling and Calculations

The molecular modeling and molecular mechanics (MM) calculations of poly-**1**-*M* were conducted with the Compass force field,[S5] as contained in the MS Modeling software (version 4.4, Accelrys, San Diego, CA) operated using a PC running under Windows XP.

The initial monomer unit structure was constructed using the crystal structure of 2-methyl-carbo[6]helicene.[S6] The main-chain helix sense of poly-**1**-*M* in THF where the negative first Cotton effect was observed at the main-chain region (380–600 nm) is assumed to be right-handed on the basis of the CD spectral pattern of the analogous L-alanine-bound helical poly(phenylacetylene) whose helix sense was determined by the direct observation of the helical structure obtained from the high-resolution atomic force microscopy (AFM).[S7] When the main-chain of poly-**1**-*M* is right-handed, it possesses an opposite, left-handed helical array of the pendants. The polymer model (40 repeating monomer units) of poly-**1**-*M* was constructed using the Polymer Builder module in the MS Modeling software. The starting main-chain geometrical parameters such as the bond lengths were defined as a 23 unit/10 turn (23/10) helix on the basis of the helical structure of a cis-transoidal poly(phenylacetylene) bearing *N*,*N*-diisopropylaminomethyl pendants determined by X-ray analysis.[S8] The dihedral angle between the main chain and the aromatic residue of the pendant (θ) was varied from 0° to 300° at 60° intervals, and the dihedral angle of the single bond (C=C–C=C) from planarity (ϕ) was set to be 140.3°,[S8] 150.7°,[S7b] 160°, and 170° (transoid) (Chart S1). The geometrical parameters for the helical poly-**1**-*M* backbone structure were fixed during the following force field optimization. The geometry optimizations were performed without any cutoff by the smart algorithm in three steps. First, the starting conformations were subject to the steepest decent optimization to eliminate the worse steric conflicts. Second, subsequent optimization until the convergence using a conjugate gradient algorithm was performed. The fully optimized polymer models were obtained by the further energy minimization using the Newton meth od with the 0.1 kcal mol^{-1} $Å^{-1}$ convergence criterion. The dihedral angles (θ and ϕ) of the optimized helical structure were 310±1° and 160°, respectively. The final right-handed helical poly-**1**-*M* model as shown in Figure 2 was reconstructed by adopting the geometry of the central monomer unit of the optimized poly-**1**-*M* structure to avoid the end-group effect.

Chart S1.

6. Enantioselective Adsorption

Enantioselective Adsorption of Poly-1s by (–)-PTrMA. A typical experimental procedure for the enantioselective adsorption of an equimolar mixture of the enantiomeric poly-**1**-*P* and poly-**1**-*M* by (–)-PTrMA is described below. A mixture of (–)-PTrMA (0.4 mg), poly-**1**-*P* (0.04 mg), and poly-**1**-*M* (0.04 mg) was dispersed in THF (2 mL) in a screw-capped sample bottle, and to this was added *n*-hexane (8 mL) at ca. 25 ˚C, affording a white precipitate of (–)-PTrMA on which poly-**1** was adsorbed. After centrifugation, the absorption and CD spectra of the supernatant solution were measured to determine the amount and ee of poly-**1** (Figure S7). In the same way, the enantioselective adsorption experiment was performed for poly-**1**-*rac* and the results are summarized in Table S1.

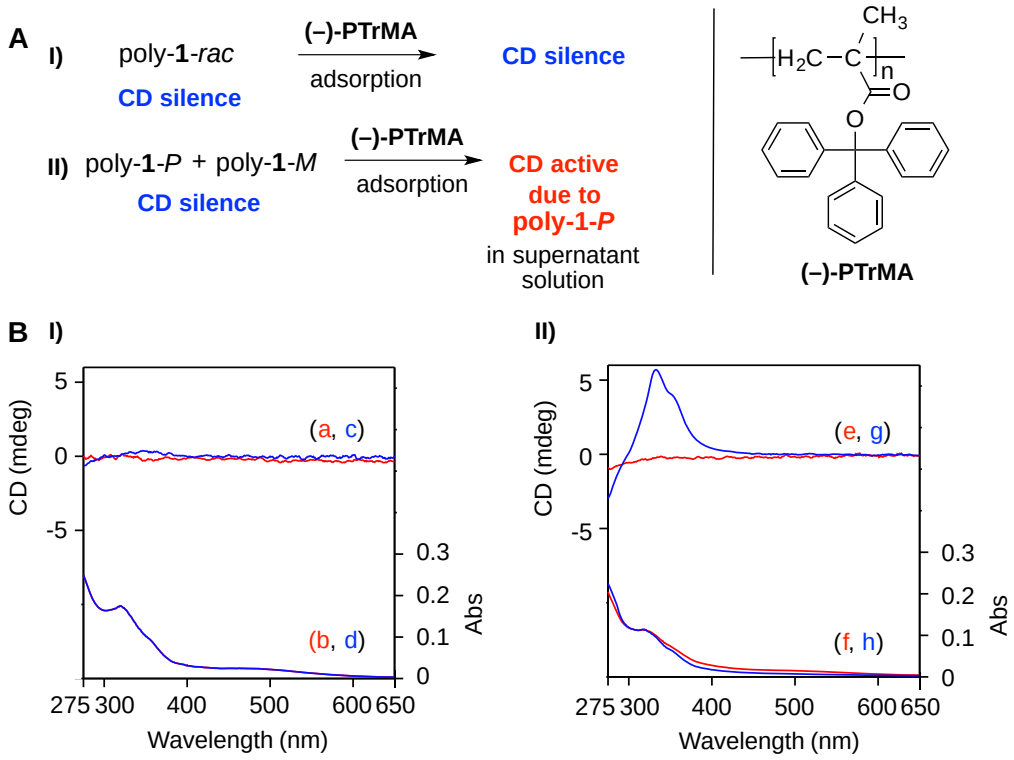

Figure S7. (A) Experimental procedures for the enantioselective adsorption of (I) poly-**1**-*rac* and (II) an equimolar mixture of poly-**1**-*P* and poly-**1**-*M* by (–)-PTrMA. (B) CD and absorption spectra of poly-**1**-*rac* (a,b, red lines) and an equimolar mixture of poly-**1**-*P* and poly-**1**-*M* (c,d, blue lines) in THF (0.04 mg/mL, 0.1 cm cell) and those of the supernatant solutions after enantioselective adsorption of poly-**1**-*rac* (e,f, red lines) and the equimolar mixture of poly-**1**-*P* and poly-**1**-*M* (g,h, blue lines) by (–)-PTrMA in THF/*n*-hexane (2:8, v/v, 5 cm cell) at 25 ˚C (see Table S1).

Table S1. Enantioselective Adsorption of Poly-1s by (–)-PTrMA

entry	analyte	yield of adsorbed analyte (%) [a]	ee of analyte in supernatant solution (%) [a]
1	poly-**1**-*rac*	94.5	<1
2[d]	an equimolar mixture of poly-**1**-*P* and poly-**1**-*M*	94.3	36.5 (*P*)

[a]Determined by absorption and CD measurements of the supernatant solution.

Enantioselective Adsorption of 1-*rac* by Poly-1-*P* or Poly-1-*M*. A typical experimental procedure for the enantioselective adsorption of **1**-*rac* by poly-**1**-*M* is described below. A solution of a racemic monomer (**1**-*rac*) in methanol (0.04 mg/mL, 1 mL) was placed into a screw-capped sample bottle containing poly-**1**-*M* (2.0 mg, powder), which had been thoroughly washed with a dibutyl ether/THF (80:20, v/v) mixture and then methanol prior to the experiments. After standing at ca. 25 ˚C for 24 h, the **1**-*rac* adsorbed on the poly-**1**-*M* was recovered by filtration and quickly washed with methanol (1 mL) to remove the racemic solution of **1** attached on the surface of the polymer. The recovered poly-**1**-*M* was placed into a screw-capped sample bottle containing methanol (5 mL), and the mixture was permitted to stand at ca. 25 ˚C for 3 h to desorb **1** adsorbed on the poly-**1**-*M*. This desorption procedure was repeated with methanol (5 mL) and then with a methanol/THF (50:50, v/v) mixture (5 mL), which almost completely desorbed **1** on the poly-**1**-*M*; the remaining **1** on the poly-**1**-*M* after the present desorption procedure was found to be negligibly small (< 0.05%) on the basis of SEC fractionation using a Tosoh TSKgel Multipore H_{XL}-M (30 cm) SEC column (THF, 0.5 mL/min) followed by HPLC analysis of **1** adsorbed on the poly-**1**-*M* after dissolving in THF. The amount and ee of **1** adsorbed on the poly-**1**-*M* were estimated by chiral HPLC using a Daicel Chiralpak IB column (0.46 (i.d.) x 25 cm, *n*-hexane/EtOH = 99:1 (v/v), 1 mL/min) equipped with UV and CD detectors. The results are summarized in Table 2.

Enantioselective Adsorption of Racemic 2 and 3 by Poly-1-*P* or Poly-1-*M*. A typical experimental procedure for the enantioselective adsorption of racemic **2** is described below. A solution of a racemic **2** in methanol (0.4 mg/mL, 1 mL) was placed into a screw-capped sample bottle containing poly-**1**-*P* (2.0 mg, powder), which had been thoroughly washed with a dibutyl ether/THF (80:20, v/v) mixture and then methanol prior to the experiments. After standing at ca. 25 ˚C for 24 h, the analyte adsorbed on the poly-**1**-*P* was recovered by centrifugation and

quickly washed with methanol (1 mL) to remove the racemic solution of **2** attached on the surface of the polymer. The recovered poly-**1**-*P* was placed into a screw-capped sample bottle containing methanol (5 mL), and the mixture was permitted to stand at ca. 25 ˚C for 3 h to desorb **2** adsorbed on the poly-**1**-*P*. This desorption procedure was repeated with methanol (5 mL) and then with a methanol/THF (50:50, v/v) mixture (5 mL). After evaporation of the solvents, the residue was subjected to SEC fractionation using a Tosoh TSKgel Multipore H_{XL}-M (30 cm) SEC column (THF, 0.5 mL/min) to recover **2**, and the amount and ee of **2** adsorbed on the poly-**1**-*P* were estimated by chiral HPLC using a Daicel Chiralpak IA column (0.46 (i.d.) x 25 cm, CH_2Cl_2, 0.5 mL/min) equipped with UV and CD detectors. The total amount of the analyte **2** obtained by this procedure was almost coincident with that estimated by the absorption spectral change of the supernatant solution during the enantioselective adsorption experiments. In the same way, the enantioselective adsorption experiment was performed for racemic **3** and the results are summarized in Table 2.

7. Supporting References

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